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Published in:
 Inorganic Chemistry

DOI:
[10.1021/ic200633a](https://doi.org/10.1021/ic200633a)

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Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2011

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Ahmed, H. M. Y., Coburn, N., Dini, D., de Jong, J. J. D., Villani, C., Browne, W. R., & Vos, J. G. (2011). Application of circular dichroism spectroscopy in the study of mixed-valence asymmetric ruthenium polypyridyl complexes. *Inorganic Chemistry*, 50(13), 5861-5863. <https://doi.org/10.1021/ic200633a>

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Application of Circular Dichroism Spectroscopy in the Study of Mixed-Valence Asymmetric Ruthenium Polypyridyl Complexes

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ABSTRACT: Circular dichroism (CD) spectroelectrochemistry is used to determine the extent of singly occupied molecular orbital delocalization in mixed-valence multinuclear complexes, specifically the mixed-valence Ru^{II}Ru^{III} states of the four diastereoisomers of $[(\text{Ru}(\text{bpy})_2)_2(\text{bpt})]^{3+}$ [**1**; bpy = 2,2'-bipyridyl and bpt = 3,5-bis(pyrid-2'-yl)-1,2,4-triazolato anion]. The complex was found to be stable to thermal racemization in the three oxidation states, but photoracemization in the Ru^{II}Ru^{II} state was observed.

Multinuclear transition-metal complexes continue to receive attention in molecular-based photonic devices, due to electroluminescence¹ and molecular wires.² Ru(II) and Os(II) polypyridyl based systems are at the vanguard of many studies because of their electrochemical and photophysical properties.³ The application of photonic devices based on these complexes requires an understanding and, ultimately, control of the nature and extent of interaction between component electroactive units. For binuclear complexes, of central concern is the strength of direct, or ligand-mediated, interaction between metal centers in their various oxidation states.

The extent of interaction in the mixed-valence state of a bimetallic complex is conventionally described using the classification proposed by Robin and Day and later Meyer and co-workers as type I, II, II/III, or III.⁴ This approach uses analysis of the intervalence (IVCT)/metal-to-metal (MMCT) charge-transfer absorption bands observed in the UV/vis–near-IR (NIR) absorption spectra of mixed-valence species, as proposed by Hush, that relates the strength of the metal-to-metal interaction (H_{ab}) and the extent of electron delocalization (α^2) with the energy, width, and molar absorptivity of the IVCT or MMCT absorption band.⁵ However, there are several limitations to this approach because the spectral changes associated with the appearance and disappearance of an IVCT or a MMCT transition upon a change of the redox state are not always easily discernible because of their generally low oscillator strength and frequent overlap with other absorption bands.⁶ In such situations, it is difficult to determine the characteristics of the absorption band and, hence, it is equally difficult to assess the degree of localization of the singly occupied molecular orbital (SOMO) in the mixed-valence state.⁴

The intrinsic chirality of octahedral ruthenium tris(diimine) complexes together with their stereochemical stability, even upon ligand substitution,⁷ has lead to the preparation and characterization of a range of chiral mono- and multinuclear Ru(II) complexes. Furthermore, the redox stability of Δ -[Ru(bpy)₃]²⁺ and its various oxidation states⁸ has allowed for characterization by UV/vis circular dichroism (CD) spectroscopy.⁹

In the present contribution, we demonstrate that CD spectroscopy can serve as a complementary analytical tool in the determination of the extent of SOMO delocalization in the mixed-valence states of binuclear complexes. In this proof of principle study, we have chosen to focus on the well-characterized binuclear complex $\{[\text{Ru}(\text{bpy})_2]_2(\text{bpt})\}^{x+}$ [**1**; bpy = 2,2'-bipyridine, bpt = 3,5-bis(pyrid-2'-yl)-1,2,4-triazolato anion, and $3 \leq x \leq 5$; Figure 1], the mixed-valence state of which, i.e., Ru^{II}/Ru^{III} ($x = 4$), has been assigned as type II/valence-localized based on analysis of its MMCT absorption band¹⁰ and, importantly, for which all four stereoisomers are available to us.¹¹

The synthesis, spectroscopic properties, and resolution in the Ru^{II}Ru^{II} redox state of the stereoisomers of **1** have been reported previously.^{10b,12} In our earlier studies, we noted that absorption and emission spectroscopy and luminescence lifetimes in both achiral and chiral solvents are identical within experimental uncertainty. Recently, Keene, Hupp, and co-workers have studied the NIR spectra in the mixed-valence state for the pairs of diastereoisomers that showed significant, albeit small, differences.¹² The absence of substantial differences between the two diastereoisomers leads to the conclusion that the interaction and delocalization is essentially the same for all four stereoisomers.

Complex **1** is stable in the Ru^{II}Ru^{II} state with respect to racemization, at room temperature in the absence of light, both in the solid state and in acetonitrile. Previously, we demonstrated that UV–vis irradiation results in photodecomposition of **1** to the corresponding mononuclear complexes.¹³ In the present study, photoracemization of **1** is observed to occur at a faster rate than decomposition; i.e., the intensity of the CD spectrum decreases without an equally substantial change in the UV/vis absorption spectrum (see the Supporting Information, Figure S17).¹⁴ The photostability of the diastereoisomers in the neutral state was determined by high-performance liquid chromatography (HPLC),¹⁵

Received: March 28, 2011

Published: May 31, 2011

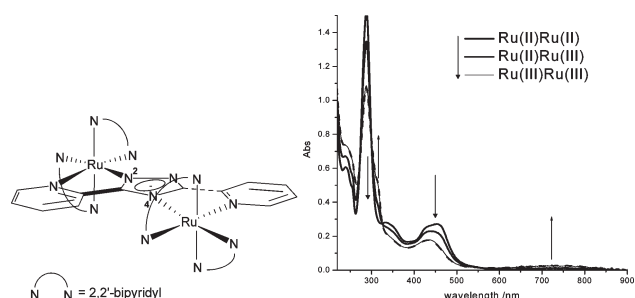


Figure 1. Left: Structure and Right: UV/vis spectroelectrochemistry of the Δ,Δ stereoisomer of **1** in acetonitrile (0.1 M KPF₆) at 298 K.

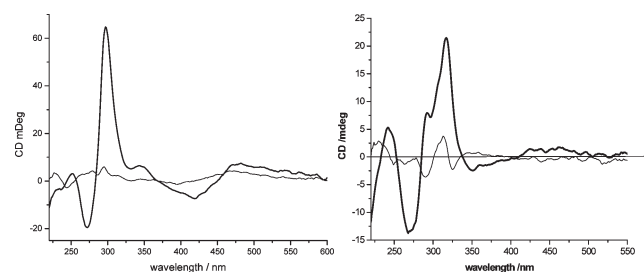


Figure 2. CD spectra of (thick line) Δ,Δ and (thin line) Δ,Δ diastereoisomers of **1** (left, Ru^{II}/Ru^{II} state; right, Ru^{III}/Ru^{III} state).

CD, and ¹H NMR spectroscopy (see the Supporting Information, Figures SI2–SI5 and SI7). These studies confirm that racemization of the enantiomers occurs with greater efficiency than decomposition.

For **1**, two Ru^{II}/Ru^{III} redox couples are observed at 1.04 and 1.34 V vs SCE. The difference between the first and second oxidation steps allows for the electrochemical generation of the Ru^{II}Ru^{III} compound, which shows an MMCT band at 1050 nm.^{10b} Oxidation of **1** to the mixed-valence state and, subsequently, to the fully oxidized Ru^{III}/Ru^{III} state results in a decrease and broadening of the absorption band at 285 nm that originates from a $\pi-\pi^*$ transition (bpy ligand), a gradual decrease of the metal-to-ligand charge-transfer (MLCT) band at ca. 450 nm, and the appearance of a broad ligand-to-metal charge-transfer (LMCT) band at 700 nm (Figure 1). Oxidation of **1** to the Ru^{III}Ru^{III} state results in only a partial depletion in the absorption bands at ca. 450 nm because of the overlap of ¹MLCT with weaker LMCT bands.¹⁰

CD spectra of **1** in the Ru^{II}/Ru^{II} state (Figure 2)¹¹ are characterized by strong Cotton effects (CEs) in the case of the homochiral stereoisomers $\Delta,\Delta/\Delta,\Delta$ and weak CEs for heterochiral stereoisomers $\Delta,\Delta/\Delta,\Delta$. The observation of the weak CEs in the CD spectra of the heterochiral stereoisomers is due to the electronic inequivalence of the two ruthenium units, one coordinated via the N2 nitrogen and the other to the N4 nitrogen of the 1,2,4-triazole bridging ligand. The CD spectra of each pair of enantiomers are mirror images, as expected.¹¹

The CD bands >300 nm are associated with ¹MLCT transitions of the (bpy)₂Ru(pyr) chromophores, whereas the CD spectrum <300 nm is dominated by intraligand (IL) transitions.¹⁶ The CD spectra of homo- and heterochiral stereoisomers (Figure 2) present the largest differences at wavelengths <350 nm, where IL transitions dominate.⁹

In contrast, to the UV–vis absorption spectra, the potential dependent changes observed in the CD spectra showed marked

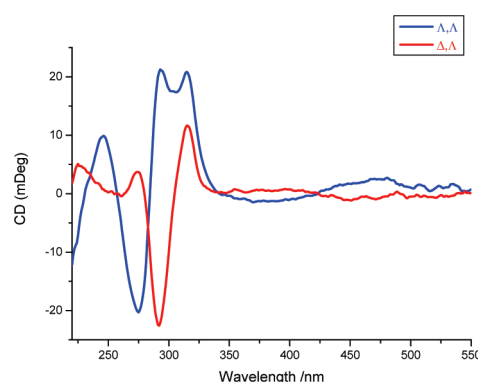


Figure 3. CD spectra of the Δ,Δ (blue), and Δ,Δ (red) stereoisomers in the mixed-valence Ru^{II}Ru^{III} state.

differences. As for the Ru^{II}Ru^{II} state, in the fully oxidized Ru^{III}Ru^{III} state (Figure 2), the homochiral stereoisomers displayed strong (and opposite) CD bands in comparison to the heterochiral isomers, where only weak CD signals, due to the imperfect cancellation of the contributions of each of the chiral centers (i.e., Δ and Δ), were observed. Importantly, a full recovery of the original UV/vis absorption and CD spectra was confirmed that the complexes are stable to thermal racemization at 293 K in all three redox states (see the Supporting Information, Figure SI6).

For the Δ,Δ isomer, oxidation of both metal centers results in a decrease in the intensity and a splitting of the $\pi-\pi^*$ transition at 300 nm, a disappearance of the CD signal at 350 nm, and a decrease in the intensity of the CD signal above 400 nm (Figure 2). For the homochiral stereoisomers, the spectrum obtained at potentials between the first and second oxidation step can be modeled accurately by a weighted sum of the CD spectrum in the fully oxidized and fully reduced states. For the heterochiral stereoisomers, the situation is more complex.

In contrast to the Ru^{II}Ru^{II} and Ru^{III}Ru^{III} redox states, in the mixed-valence state (Ru^{II}Ru^{III}), all four diastereoisomers of **1** show CD spectra of comparable intensity in the UV/vis range (Figure 3). For the homochiral stereoisomers, the strong CD signal is expected; however, for the heterochiral stereoisomers, the strong CD signal holds considerable implications for localization of the “hole” in the mixed-valence state and the extent of electron exchange between the metal centers.

The CD spectrum of the mixed-valence heterochiral Ru^{II}Ru^{III} species is a superposition of the CD spectra of the homochiral Ru^{II}Ru^{II} and Ru^{III}Ru^{III} (Figure 2) complexes. In order to rationalize this observation, limiting cases for electron delocalization in the mixed-valence compound can be considered.

In the first limiting situation, the SOMO is delocalized over both metal centers (i.e., type III interaction). In this case, in the mixed-valence state, the heterochiral complexes should have near-complete cancellation of the CD spectra of each center as observed for the Ru^{II}Ru^{II} or Ru^{III}Ru^{III} states. This is not observed in the present case. A second limiting situation is complete localization of the SOMO on one of the ruthenium centers.

In the present case, the N2- and N4-bound redox centers are inequivalent. This difference is associated with the better σ -donor properties of the N2 binding site with the N2-bound Ru(II) center oxidized first, and the N4 site at 80 mV higher potential.^{10b} This redox asymmetry would result, where the SOMO is localized on a single metal center, in the N²Ru^{II}–N⁴Ru^{III}

species the major species observed in solution (>75%) and the $\text{N}^2\text{Ru}^{\text{III}}-\text{N}^4\text{Ru}^{\text{II}}$ species the lesser species (<25%). Hence, in the case where the SOMO is localized but hopping between the metal centers occurs, then the equilibrium will be in favor of one center being oxidized over the other. The MMCT absorption band for **1** in the mixed-valence state, which yields values of $H_{\text{ab}} = 700 \text{ cm}^{-1}$ and α^2 of 1.6×10^{-2} , suggests that there is considerable electronic communication between the two metal centers.¹⁰ However, the CD spectra of the Ru^{II} and Ru^{III} redox states are distinctly different, and in the mixed-valence state, the CD spectrum of the Ru^{II} center will not cancel that of the Ru^{III} state. Hence, the observation of strong CD spectra for both homo- and heterochiral complexes confirms that, despite there being sufficient interaction between the metal centers to allow for optical electron transfer, the complex is valence-localized in the mixed-valence state and the SOMO is localized on only one of the two sites (i.e., $\text{N}2$).

In conclusion, in the present study, the utility of CD spectroscopy in gaining a deeper insight into SOMO localization/delocalization in nonsymmetric mixed-valence multinuclear complexes is demonstrated. For the type II complex **1**, the UV/vis absorption spectra of the four diastereoisomers are essentially identical in all three redox states examined. By contrast, the CD spectra show that the SOMO orbital is based on the $\text{N}2$ center and, hence, the optical electron transfer is directional ($\text{N}4$ to $\text{N}2$).

CD spectroelectrochemistry of non-symmetric dinuclear compounds may be of special interest in cases where the presence of an intervalence band has not been established or is unclear, providing further information about the nature of the mixed-valence state in these complexes, in particular, establishing whether or not the metal–metal interaction is sufficient to result in SOMO delocalization in the ground state. Importantly, it should be noted that although we have chosen to use a dinuclear complex in which the two metal centers are nonequivalent, the approach should be applicable to systems in which the centers are equivalent. In this latter case, the expected observations are, however, different from that described above. The heterochiral stereoisomers would not exhibit a CD signal in any oxidation state. The homochiral stereoisomers would yield the necessary information, however in the localized there would be an effective superposition of the CD spectrum of the oxidized and reduced states, while in the delocalized state, the mixed-valence complex would have a different spectrum compared with the fully reduced and fully oxidized forms.

■ ASSOCIATED CONTENT

Supporting Information. HPLC and ^1H NMR spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

The authors acknowledge The Netherlands Science Organization (W.R.B.) and the Science Foundation Ireland (Project 07/SRC/B1160) for financial support (to D.D. and J.G.V.).

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